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A novel approach to synthesize carboxymethyl guar gum via friedel craft acylation method

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ABSTRACT

Carboxymethyl guar gum (CMGG) synthesized via Friedel Craft Acylation using $FeCl_3$ and $AlCl_3$ as Friedel Craft catalyst. Also the effect of phase transfer catalyst tetra ethyl ammonium bromide (TEAB) on the degree of substitution (DS) was monitored. The reaction parameter like temperature, reaction time etc. was optimized. The DS of reaction product was measured by Amberlite IRA 96 anion exchange resin. Maximum DS of 0.7 was obtained. CMGG was characterized by Fourier Transform Infrared spectroscopy (FTIR).

KEYWORDS

Guar gum (GG);
Friedel craft acylation;
Carboxymethylation;
FTIR.

INTRODUCTION

Guar gum (GG) is galactomannan, extracted from the ground endosperm of *cyamopsis tetragonolobus*, is a high molecular weight hydrocollodial hetero polysaccharide composed of galactose and mannose units, which are linked by glycosidic bonds[1,2].

The general structure of guar gum is as shown in Figure 1, which consists of a linear backbone of β (1, 4) – linked D-mannose units with various amounts of α (1,6) – linked D- galactose side chains. The mannose to galactoseratio is 2:1. The average molecular weight of guar gum is between 220,000 - 300,000[3-7]. Guar gum is soluble in water but insoluble in hydrocarbon, fats, alcohol, esters, and ketones[8]. The solution of guar gum in water has the highest viscosity amongst all the natural polysaccharide discovered till the date[9]. Further it has better biodegradability and bio-compatibility compare to other natural polysaccharides. Due to these properties guar gum finds applications in industries like mining, textiles, explosives, paper, petroleum, cosmetic industry, food industry etc[10]. GG were cost effective, nontoxic, noncorrosive, ecofriendly and abundantly

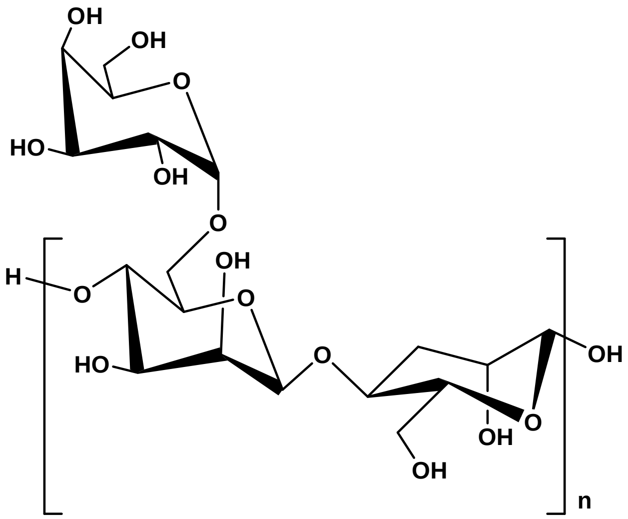

Figure 1 : Structure of guar gum

available biopolymer. Further the biodegradability and bio-compatibility of guar gum encourage the researchers for its use in pharmaceutical industries.But due to the uncontrollable viscosity of the guar gum solution, uncontrollable rate of hydration, instability of its solutions for longer time and susceptibility to microbial contamination restricts its use in pharmaceutical industries[11-14].

To overcome these draw back guar gum should be chemically modified. Modified guar gum by one or more reactions like, depolymerization, oxidation, hydroxyalkylation, cyanoethylation, quarternization and sulphation was reported[15-19]. GG derivatives like O-(2-hydroxyethyl), O-(2-hydroxypropyl) were reported but this fails to more or less extent in getting used in pharmaceutical industries due to the introduction of substitutes groups to the galactomannan polymer which increased branching and entanglements and therefore higher viscosity[8]. Modified natural polysaccharides like carboxymethyl cellulose, carboxymethyl starch finds application in pharmaceutical industries[20,21].

Other natural polysaccharides were carboxymethylated by conventional method using NaOH and Na-salt of chloroacetic acid[22-25]. In organic chemistry no.of compound synthesize by well-knownFriedel Craft reaction, using $AlCl_3$ and $FeCl_3$ as catalyst.But there was no work reported on carboxymethylation of natural polysaccharide via Friedel Craft acylation reaction. There so, we synthesized carboxymethyl guar gum via Friedel Craft acylation reaction using $AlCl_3$ and $FeCl_3$ as catalyst. The reaction was carried out in heterogeneous phase, so quaternary salt of ammonia was used as phase transfer catalyst.

There so, in the present work guar gum was carboxymethylated by Friedel craft acylation methods by using $AlCl_3$ and $FeCl_3$ as a Friedel craft catalyst, while tetra ethyl ammonium bromide used as phase transfer catalyst. Effect of $AlCl_3$ and $FeCl_3$ on reaction was studied. The effect of time, temperature, solvent were also studied and compared with other conventional method to synthesized CMGG were also studied.

EXPERIMENTAL

Materials and methods

Guar gum, acetyl chloride, ferric chloride, aluminium chloride and tetra ethyl ammonium bromidewere purchased from Sigma- Aldrich. Solvents likeethanol and iso propyl alcohol were of A.R. grade. All other reagents were of LR grade.

Carboxymethylation of guar gum

Guar gum was carboxymethylated by Friedel craft acylation method by using two different catalyst viz. $FeCl_3$, $AlCl_3$, phase transfer catalyst like tetra ethyl ammonium bromide and iso propyl alcohol as a solvent.

Friedel craft acylation

Purified guar gum was dispersed in 150 ml of iso propyl alcohol, in 250 ml round bottom flaskflask equipped with a magnetic stirrer. After the gum was well dispersed, catalyst $AlCl_3$ and the phase transfer catalyst tetraethyl ammonium bromide was added. After that acetylating agent (acetyl chloride, 5 ml) was added and the reaction is continued at room temperature with constant stirring for 5 hrs. After completion of reaction carboxymethyl guar gum was precipitated with the help of methanol and the precipitated product was purified.

Purification of modified guar gum

The insoluble CMGG in its acidic form was dialyzed against distilled water for 3 days. The suspension was precipitated with ethanol washed with solvent exchange (ethanol, acetone, ether) and dried under reduced pressure.

Degree of substitution in modified guar gum

The degree of substitution (DS) is the average number of sodium carboxymethyl groups bound per anhydroglucose unit. This method is used to determine the number of substituent groups added to the guar gum backbone. From the DS one can find how many hydroxyl groups isconverted into carboxymethyl groups. Degree of substitution markedly affects the properties of the compound.

1 gm. of CMGG was dissolved in known amount of water. Then this solution was passed through regenerated Amberlite IRA 96 anion exchange resinno. of times till it become acidic. Then the solution was divided into two equal parts labeled as solution 1 and solution 2. The exhausted resin was regenerated by passing 1 N HCl solution (3-4 times) followed by wash-

ing with distilled water to remove any excess acid.

Solution1was taken into previously weighed beaker. Evaporate water by heating on a hotplate and cool it into desiccator and weigh it again. Find the weight of residue left in the beaker. Find out concentration by evaporation.

Solution 2 was titrated against a standard solution of NaOH. Note down the burette reading and find out the degree of substitution by following equation.

$$\mathbf{DS} = \frac{0.162\ \mathbf{B}}{1 - 0.58\ \mathbf{B}}$$

Where, $\mathrm{B} = \frac{\text{Volume of 1N NaOH used}}{\text{Weight of sample}}$

Characterization of modified guar gum

The resulting products were characterized by FTIR spectroscopy using Perkin Elmerspectrum GX instrument, by the KBr pallet method.

RESULT AND DISCUSSION

Carboxymethyl guar gum (CMGG)

Carboxymethylation of guar gum is a consecutive two-step reaction proceeding with a generation of anacylium ion. The acylium ion is formed by the removal of halide by the Lewis acid catalyst $AlCl_3$. This acylium ion reacts with free hydroxyl group of guar gum to generate carboxymethyl guar gum.

Effect of catalyst

Effect of catalyst on DS was tabulated in TABLE 1. It can be concluded from the table that high DS was obtained by using $AlCl_3$ compared to $FeCl_3$ as catalyst.

TABLE 1 : Effect of catalyst on DS

Catalyst	Degree Of Substitution
$AlCl_3$	0.7
$FeCl_3$	0.5

Effect of time

The effect of time on reaction was tabulated in TABLE 2. Reaction was carried out for 4, 5 and 6 hrs. The maximum DS was obtained by carrying out reaction for 5 hrs. using $AlCl_3$ as catalyst.

TABLE 2 : Effect of time

Time (in hrs.)	Catalyst	DS
4	AlCl3	0.31
	FeCl3	0.20
5	AlCl3	0.7
	FeCl3	0.58
6	AlCl3	0.65
	FeCl3	0.44

FTIR analysis

The IR spectrum of guar gum and carboxymethyl guar gumwas shown in Figure 2 and Figure 3 respectively. The IR spectrum of carboxymethyl guar gum shown a reduced intensity of the absorption band located at 3439 cm^{-1}, as compared to guar gum IR spectrum due to -OH is stretching, indicating that some -OH group were carboxymethylated. The C-O sym-

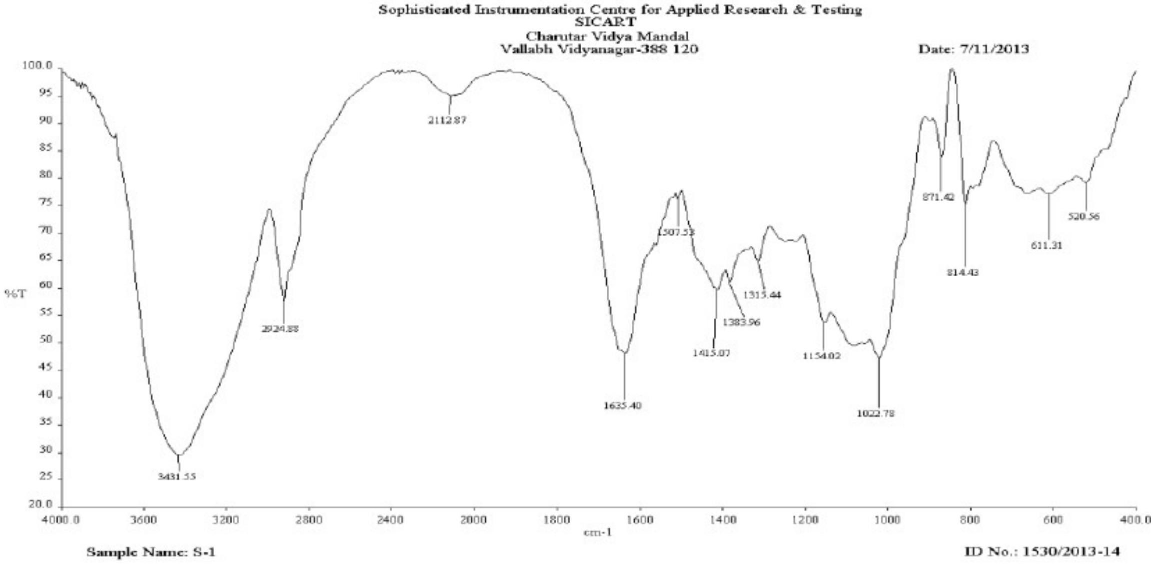

Figure 2 : IR spectra of GG

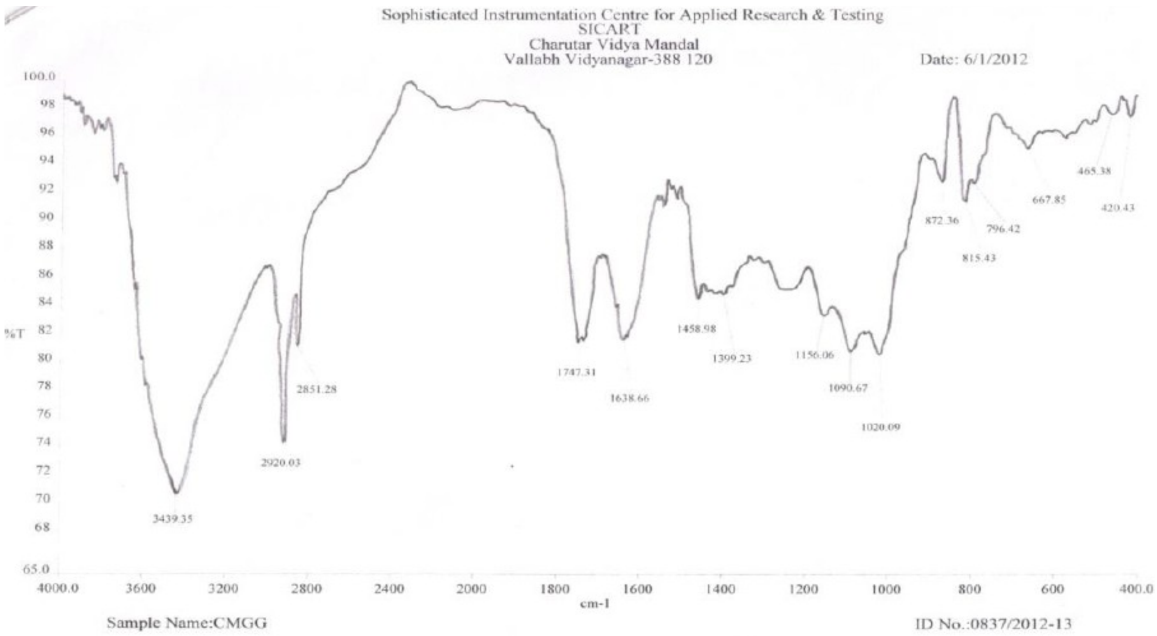

Figure 3 : IR spectra of CMGG

metrical and asymmetrical and vibrations at a frequency of 1090.67 cm^{-1} and 1156.06 cm^{-1} confirms the incorporation of the carboxymethyl group on to the guar gum molecule, which is absent in the guar gum spectra.

CONCLUSION

The carboxymethylation of guar gum carried out successfully via Friedel Craft acylation reaction. Maximum DS of 0.7 was obtained carrying reaction for 5 hrs. using $AlCl_3$ catalyst. Carboxymethylation improves the properties of guar gum especially, rate of hydration, viscosity and susceptibility to microbial contaminations. This modified guar gum finds its application in the pharmaceutical industry as a drug binder or as a drug carrier.

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